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First Named Inventor	:	Krzysztof Matyjaszewski
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DECLARATION UNDER 37 C.F.R. 1.132

I, Nicolay V. Tsarevsky, hereby declare and state as follows:

I have earned a Ph.D. in Chemistry from Carnegie Mellon University in 2005 and an M.S. Chemical Physics and Theoretical Chemistry from University of Sofia in 1999 and am now a Visiting Assistant Professor in the Department of Chemistry of Carnegie Mellon University.

I am listed as an inventor on United States Patent No. 6,624,262 and on three pending patent applications, including the above referenced United States patent application No. 10/684,137 and two additional international patent applications designating the United States of America.

I have also authored and coauthored a significant number of articles on polymers and polymerization processes, including the following publications related to transition metal catalyzed polymerizations such as atom transfer radical polymerization, controlled radical polymerization in aqueous systems, functional polymers:

• "Synthesis of Degradable Miktoarm Star Copolymers via Atom Transfer Radical Polymerization", Gao, H., Tsarevsky, N. V., Matyjaszewski, K., Macromolecules, 2005, 38(14).

• "Quantifying Vinyl Monomer Coordination to CuI in Solution and the Effect of Coordination on Monomer Reactivity in Radical Copolymerization", Braunecker, W. A., Tsarevsky, N. V., Pintauer, T., Gil, R. R., Matyjaszewski, K., Macromolecules, 2005, 38(10), 4081-8.

• "Step Growth "Click" Coupling of Telechelic Polymers Prepared by Atom Transfer Radical Polymerization", Tsarevsky, N. V., Sumerlin, B. S., Matyjaszewski, K., Macromolecules, 2005, 38(9), 3558-61.

• "Combining Atom Transfer Radical Polymerization and Disulfide / Thiol Redox Chemistry: A Route to Well-Defined (Bio)degradable Polymeric Materials", Tsarevsky, N. V., Matyjaszewski, K., Macromolecules, 2005, 38(8), 3087-92.

• "Grafting of Well-defined Polymers from the Surface of Functionalized Single-Walled Carbon Nanotubes via Atom Transfer Radical Polymerization and Visualization of the Polymer-Nanotube Hybrids by Atomic Force Microscopy", Tsarevsky, N. V., Wu, W., Hudson, J. L., Kowalewski, T., Tour, J. M., Matyjaszewski, K., Polym. Prepr., 2005, 46(1), 203-4.

• "Towards Understanding Monomer Coordination in Atom Transfer Radical Polymerization: Synthesis of [CuI(PMDETA)(pi-M)][BPh4] (M = Methyl Acrylate, Styrene, 1-Octene, and Methyl Methacrylate) and Structural Studies by FT-IR and 1H NMR Spectroscopy and X-ray Crystallography", Braunecker, W. A., Pintauer, T., Tsarevsky, N. V., Kickelbick, G., J. Organometal. Chem., 2005, 690, 916-24.

• "Deactivation Efficiency and Degree of Control Over Polymerization in ATRP in Protic Solvents", Tsarevsky, N. V., Pintauer, T., Matyjaszewski, K., Macromolecules, 2004, 37(26), 9768-78.

• "Well-defined (Co)polymers with 5-Vinyltetrazole Units via Combination of Atom Transfer Radical (Co)polymerization of Acrylonitrile and "Click Chemistry"-Type Postpolymerization Modification", Tsarevsky, N. V., Bernaerts, K. V., Dufour, B., Du Prez, F. E., Matyjaszewski, K., Macromolecules, 2004, 37(25), 9308-13.

• "Reversible Redox Cleavage/Coupling of Polystyrene with Disulfide or Thiol Groups Prepared by Atom Transfer Radical Polymerization", Tsarevsky, N. V., Matyjaszewski, K., Macromolecules, 2002, 35(24), 9009-14.

• "Nanostructured Carbon Arrays from Block Copolymers of Polyacrylonitrile", Kowalewski, T., Tsarevsky, N. V., Matyjaszewski, K., J. Am. Chem. Soc., 2002, 124(36), 10632-3.

• "Synthesis of Styrene-Acrylonitrile Copolymers and Related Block Copolymers by Atom Transfer Radical Polymerization", Tsarevsky, N. V., Sarbu, T., Goebelt, B., Matyjaszewski, K., Macromolecules, 2002, 35(16), 6142-8.

• "Radical Thermo- and Sonopolymerization of Methyl Methacrylate Initiated by Iodobenzene I,I-diacetate", Georgiev, G. S., Kamenska, E. B., Tsarevsky, N. V., Christov, L. K., Polymer International, 2001, 50, 313-8.

• "Atom Transfer Radical Polymerization of n-Butyl Methacrylate in an Aqueous Dispersed System: A Miniemulsion Approach", Matyjaszewski, K., Qiu, J., Tsarevsky, N. V., Charleux, B., J. Polym. Sci.: Part A: Polym. Chem., 2000, 38, 4724-34.

I have read and understood United States Patent Application No. 10/684,137 (the "Subject Application") including the claims. I have also read and understood the cited prior art references United States Patent No. 3,037,004 issued to Simone et al. ("Simone") and United States Patent No. 5,807,937 issued to Matyjaszewski et al (the "'937 patent"). The Subject Application discloses and claims a catalytic polymerization process, comprising reacting free radically (co)polymerizable acidic monomers utilizing a suitable transition metal complex as a catalyst, wherein the suitable transition metal complex has acidity constants of the protonated ligand greater than 10^{-4} and conditional disproportionation constant than less than 1000.

The process of the Subject Application is also be invention is also directed toward a method of determining the suitability of a transition metal complex for use in a catalytic reaction, such as, but not limited to, atom transfer radical polymerization ("ATRP"), atom transfer radical addition ("ATRA"), atom transfer radical cyclization ("ATRC") and other catalytic redox processes. I understand and believe one skilled in the art would understand that the catalysts for ATRP of acidic monomers may also be used in other catalytic atom transfer reactions such as ATRA and ATRC. The catalyst must be able to sufficiently extract a radically transferable atom or group from an initiator to allow addition of the monomer (olefinically unsaturated compound).

A feature of controlled polymerization processes is the existence of an equilibrium between active and dormant polymerization species. In an uncontrolled

polymerization process, the active polymerization species is formed and continues to grow until an irreversible termination reaction occurs. Conversely, in controlled polymerization processes, an exchange between the active and dormant polymerization species allows for slow but substantially simultaneous growth of all chains. Therefore, in controlled polymerization processes, the polymer chains cycle between an active species and a dormant species. As described above, there is no exchange or equilibrium between active and dormant species in the uncontrolled polymerization processes, such as disclosed in Simone.

In order to maintain the equilibrium necessary to polymerize in acidic conditions such as with acidic monomers with ATRP or to perform an ATRC or ATRA reaction in acidic conditions, it is necessary to have a suitable transition metal catalyst. The '937 patent clearly describes many transition metal complexes that will function in ATRP reactions. However, in the Subject Application, we describe the properties of suitable transition metal catalysts for reactions under acidic conditions. The '937 patent is a pioneering patent that broadly describes potential monomers and catalysts that may be used with ATRP. The exemplary ligands include bipyridine, derivatives of bipyridine to increase the solubility of the catalyst and other ligands. As described in the Subject Application, the transition metal catalysts that are formed from these ligands are not suitable for reactions under acidic conditions such as with acidic monomers.

The Subject Application in one embodiment is directed toward a catalytic process, comprising reacting free radically (co)polymerizable acidic monomers utilizing a suitable transition metal complex as a catalyst. A catalyst is suitable for the reaction if the interactions of the catalyst with the reaction media and the reaction components do not prevent the catalyst from being active in the desired reaction. For acidic monomers, the exemplified catalysts of the '937 patent are not suitable catalysts, nor does the '937 patent teach how to select a suitable catalyst from the range transition metal and ligand combinations described in the '937 patent.

For example, as taught in the Subject Application, a suitable catalyst may have a combination of the following properties: at least partially soluble in the reaction media, possess a low redox potential, stability towards ionic species, low propensity to disproportionation, and sufficient conditional metal-radically transferable atom or group phylicity to act as a catalyst in the reaction media.

Ligands having such properties are a narrow set of ligands compared to the set of ligands described in the '937 patent and these parameters are not taught in the '937 patent or elsewhere prior to filing of the Subject Application. One skilled in the art would not find these properties obvious from the disclosure of the '937 patent. The Subject Application (see Paragraphs [0063] to [0074] and Example 4A, and the attached article entitled *Factors Determining the Performance of Copper-Based ATRP Catalysts and Criteria for Rational Catalyst Selection* analyze catalysts exemplified in the '937 patent to show that they do not have the properties described for a suitable catalyst.

I further declare that all statements made herein are true and that all statements made on information and belief are believed to be true; and further that these statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statement may jeopardize the validity of the application or document or any registration resulting therefrom.

Nicolay V. Tsarevsky

May 11, 2006
Date